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## Investigating Dechlorane Plus (DP) distribution and isomer specific adsorption behavior in size fractionated marine sediments

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## HIGHLIGHTS

- DP was first time to be investigated in different particle size fractions.
- $f_{anti}$  correlated with organic carbon content.
- Syn-DP was preferentially adsorbed by organic carbon.

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## ABSTRACT

In this study, Dechlorane Plus (DP) concentrations were analyzed in marine sediments (depth: ~10 cm) from two Korean industrial bays. Two sediments were fractionated into 5 sizes by using gravitational split-flow thin fractionation technique and DP distribution was investigated in different particle size fractions. Elevated DP levels in surface sediments were observed at the site closest to land and industrial area. The highest concentrations of DP were detected in the finest grain-size (<10  $\mu\text{m}$ , 451.2 and 149.9 pg/g dry weight for the two bays). The fraction of *anti*-DP to the total DP ( $f_{anti}$ ) in the two fractionated samples increased with reduced grain-size and significantly correlated with organic carbon content (OC), which can be caused by preferential adsorption of *anti*-DP or higher biodegradation rates of *syn*-DP in the fine particles. To provide insight into such mechanism, simulated experiments were conducted using activated charcarbon (ACC) to adsorb DP dissolved in methanol and molecular descriptors of both isomers were estimated using Gaussian 03. The adsorption results revealed that *syn*-DP was preferentially adsorbed by ACC, suggesting *syn*-DP is more hydrophobic than *anti*-DP. The preferential adsorption of *syn*-DP by ACC also supported the hypothesis that the enrichment of *anti*-DP was more likely due to preferential biodegradation of *syn*-DP in the sediment. Molecular characterization of *anti*-DP and *syn*-DP showed that *syn*-DP had a higher dipole moment, slightly larger Van der Waals volume, but smaller maximal diameter, which might explain its higher uptake rate in biota.

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## 1. Introduction

Dechlorane Plus (DP,  $\text{C}_{18}\text{H}_{12}\text{Cl}_{12}$ ) is a highly chlorinated flame retardant that has been primarily used in electrical wires and cables, computer connectors, and plastic roofing materials as a replacement for Dechlorane (Mirex,  $\text{C}_{10}\text{Cl}_{12}$ ) (OxyChem, 2004). This product has been manufactured for more than 40 years by OxyChem (Niagara Falls, NY) and annual production has been estimated to be as high as 5,000 tons (Sverko et al.,

2011). Another manufacturing facility is located in Anpon, China, with an annual production of 300–1000 t since 2003 (Wang et al., 2010). Since its first discovery in Great Lakes (Hoh et al., 2006), DP has become a ubiquitous pollutant in air, water, soil, and sediment (Sverko et al., 2011). Despite its high molecular weight and octanol–water partition coefficient ( $\log K_{OW} = 9.3$ , US EPA, <http://www.epa.gov/hpv/pubs/summaries/dechlorp/c15635.pdf>), bioaccumulation of DP has been readily observed in fishes, birds and their eggs (Gauthier et al., 2007; Kang et al., 2010).

In South Korea, several previous studies have revealed high levels of DP contamination in urban areas, where no DP was manufactured. Qiu and Hites (2008) have observed that DP concentrations ( $1.4 \pm 1.5$  ng/g bark) in tree bark from Hanam, South Korea were comparable to or higher than those in the northeastern United States. Kang et al. (2010) reported DP concentrations in fish collected from a Korean urban area were 25 times higher than those from

Abbreviations: DP, Dechlorane Plus; OC, organic carbon; ACC, activated char carbon;  $K_{OW}$ , octanol–water partition coefficient; PAHs, polycyclic aromatic hydrocarbons; PCBs, polychlorinated biphenyls; PCDD/Fs, polychlorinated dibenzo-*p*-dioxins and dibenzofurans; BAF, bioaccumulation factor.

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rural areas. Therefore, further study on DP in South Korea is of great significance to elucidate source and fate of these DP.

Sediments are known to be an important final sink for many hydrophobic organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). DP is characterized by a large  $\log K_{OW}$  value, which promotes its partitioning into sediments. Organic materials adsorbed on sediments are the sole food source for many benthic organisms, burrowing invertebrates, and filtering organisms (Connolly, 1991; Harkey et al., 1994). It is known that physicochemical properties of the sediment (e.g., particle size and organic carbon content) play important roles in its abiotic and biotic interactions with the chemicals (Brannon et al., 1991; Lee et al., 2006). For instance, absorption experiments have shown that PAHs, PCBs and PCDD/Fs distribute preferentially into fine, organic-rich particles (Kukkonen and Landrum, 1995; Lee et al., 2006). Most of the previous studies, however, have only restricted to binary comparison of sandy ( $>63\ \mu\text{m}$ ) and muddy sediments ( $<63\ \mu\text{m}$ ). However, particles of diameter  $63\ \mu\text{m}$  are too large to be consumed by benthic organisms. For example, *Diporeia* and *Zebra mussels* more readily ingest sediment particles that are  $2\text{--}20\ \mu\text{m}$  in diameter (Klump et al., 1987). Therefore, it is interesting to examine DP distribution in different grain-size sediments, especially in smaller size fractions that animals ingest.

Two stereoisomers, *syn*-DP and *anti*-DP exist and commercial products contain a mix of the two. The two isomers have been investigated and results published indicate differences in their environmental transport and fates. Compared to commercial products, enrichment of *anti*-DP in the sediment was observed in many studies, indicating that the two isomers undergo different physical, chemical or biological processes in the sediment (Sverko et al., 2011). In contrast, Yang et al. have found that the fraction of *anti*-DP/total DP ( $f_{anti}$ ) in the sediment decreased with the distance from the source (Yang et al., 2011). Similarly, Möller et al. (2010) observed a decreased  $f_{anti}$  with decreasing northern latitude in the air samples. Both studies assumed that *anti*-DP isomer is more vulnerable to photo-degradation during long-range atmosphere transport (LRT). However, photo-degradation might not be important to particulate-bound DP due to light shielding effect by aerosols (Koester and Hites, 1992). A recent study showed that the photolysis difference between *syn*-DP and *anti*-DP was negligible in *n*-nonane under the irradiation of xenon lamp (Wang et al., 2013). Furthermore, different uptake rates and bioaccumulation behavior of both isomers was also observed between *syn*-DP and *anti*-DP (Tomy et al., 2008). Uptake rates and bioaccumulation factor (BAF) of *syn*-DP were 3 times higher than that of *anti*-DP, and were found to be 0.045 nmmol/day and 5.2 for *syn*-DP and 0.018 nmmol/day and 1.9 for *anti*-DP; respectively. All these facts indicate that environmental and biological fates of DP are isomer specific, which are likely consequences of different physicochemical properties of *anti*-DP and *syn*-DP. However, to date, few systematic investigations on the difference between *anti*-DP and *syn*-DP have been made in sediments.

The objectives of this study were to: (1) investigate the DP concentration in Korean marine sediments and characterize DP distribution in different particle size fractions; (2) examine the  $f_{anti}$  profile in the whole sediments and different particle size fractions; (3) tentatively explain the stereoisomer specific environmental and biological fates by exploring the physicochemical properties of the *anti*-DP and *syn*-DP based on accessible experimental and computational data. Specifically, we examined the concentration of DP in the marine sediments from Busan Bay and Pohang Bay, both of which are coastal bays near well-developed industrial areas. To investigate DP distribution in various particle size, mud-sized ( $<63\ \mu\text{m}$ ) sediments were fractionated by size using a newly developed gravitational split-flow thin fractionation technique (GSF) (Moon et al., 2005), and the DP levels were analyzed as a function of particle size. To explain the difference between *anti*-DP and *syn*-DP, we calculated isomer-specific molecular descriptors using Gaussian 03 suite of programs (Revision C.02) and conducted further

experiments to simulate the sorption process of the two isomers in the sediment. To our knowledge, this is the first study to evaluate the DP distribution in sediment fractions with different particle sizes and the first attempt at investigating the transport behavior of *anti*-DP and *syn*-DP.

## 2. Materials and methods

### 2.1. Sediment collection

Marine sediments samples were collected from Busan Bay and Pohang Bay area at locations shown in Fig. 1. Specifics of sampling information were listed in Table S1 in the Supporting information (SI). Six archived sediment samples (depth:  $\sim 50\ \text{cm}$ ) were collected from Pohang Bay and five were collected from Busan Bay using a core sampler in 2003. In this study, the sediment (depth:  $\sim 10\ \text{cm}$ ) was sectioned and analyzed. The city of Pohang, located along the eastern coastline of Korea, has one of the largest steel making complexes in the world. Busan Bay is surrounded by several industrialized cities, where many industrial plants and two large shipyards are operating. Domestic and industrial waste water are discharged via several streams to the bays. All sediment cores were stored below  $-20\ ^\circ\text{C}$  until the particle fractionation and instrumental analysis.

### 2.2. Particle fractionation by GSF technique

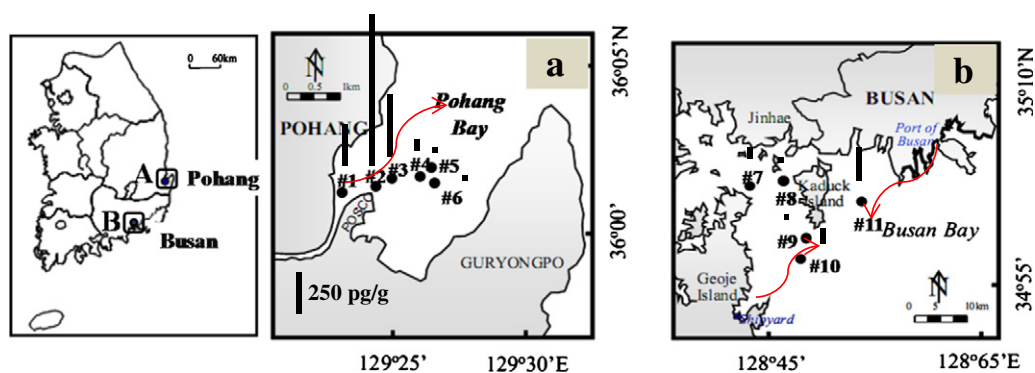
Particle fractionation of two sediment cores was accomplished through our developed GSF (Moon et al., 2004, 2005). Sediment samples (200 g, density:  $2.1\ \text{g/mL}$ ) were suspended in 40 L of ultrapure water ( $>18\ \text{M}\Omega$ ) containing 0.02%  $\text{NaN}_3$  as a bactericide and 0.1% FL-70 as a surfactant. The suspensions were then sieved with a 270-mesh sieve ( $53\ \mu\text{m}$  pores) and a 325-mesh sieve ( $44\ \mu\text{m}$  pores) in wet condition. Forty liters of the solution passing through both the 270 and 325-mesh sieves were collected and continuously stirred with a magnetic stir bar to avoid particle settlement. The fractions which were retained by the sieves were also collected as the size of  $>53\ \mu\text{m}$  and  $44\text{--}53\ \mu\text{m}$ . The solution was then introduced into the GSF by a peristaltic pump. Finally, fractionated sediment samples were obtained in the following size fractions:  $>53\ \mu\text{m}$ ,  $44\text{--}53\ \mu\text{m}$ ,  $10\text{--}44\ \mu\text{m}$ ,  $5\text{--}10\ \mu\text{m}$ , and  $<5\ \mu\text{m}$ . Organic carbon (OC) and black carbon (BC) contents were measured for each fraction following the method described in the SI.

### 2.3. Molecular modeling

Molecular modeling was performed with the Gaussian 03 (Gaussian Inc.). After the geometry optimization of *anti*-DP and *syn*-DP, a user-friendly Gaussian based Multiwfn program was used to view the molecular size (Lu and Chen, 2012).

### 2.4. Analysis and QA/QC

Details of DP analysis were given in the SI. Briefly, dried samples (approximately 10 g) were Soxhlet-extracted for 24 h with dichloromethane (DCM). Cleanup was performed with concentrated sulfuric acid and multilayered silica columns. Individual standards of *syn*- and *anti*-DP ( $50\ \mu\text{g/mL}$ , in toluene) were supplied by Wellington Laboratories (Guelph, ON, Canada).  $^{13}\text{C}$ -labeled *anti*-DP and *syn*-DP (Cambridge, MA, USA) was spiked as internal standard and  $^{13}\text{C}$ -labeled PCB 169 (Cambridge, MA, USA) was added as recovery standard. DP was analyzed on a gas chromatograph (Hewlett-Packard 6890) coupled to a high-resolution mass spectrometer (Jeol JMS-700 T). Mass-to-charge ( $m/z$ ) ions monitored for the compounds in this study were 271.8102/273.8072 (qualifier) and 651.7142/653.7113 (quantifier) for both *syn*- and *anti*-DP. The ions of  $m/z\ 661.7/663.7$  were monitored for  $^{13}\text{C}$ -labeled *anti*-DP and *syn*-DP. Field blanks were obtained by bringing  $\text{Na}_2\text{SO}_4$  to the sampling sites and then processed alongside with the



**Fig. 1.** Location of sediment sampling sites and concentration of DP (pg/g d.w.) in sediment samples demonstrated by heights of solid bars. Two sediment samples for fractionation were collected at #3 and #10. (a) Pohang Bay, (b) Busan Bay. "POSCO" is the steel making plant in Pohang Bay and "Shipyard"/"Port of Busan" are primary industries in Busan Bay. The arrow in red represents the suggestive water current.

sediment samples. Method detection limits (MDLs), calculated as three times the standard deviation of triplicate field blanks, were 1.3 pg/g d.w. and 1.6 pg/g d.w. for *syn*-DP and *anti*-DP; respectively. Recoveries of DP in the sediment samples ranged from 70 to 97%. To assess the intra- and inter-day variation of our DP analysis, an in-house reference material was used, which was obtained by mixing sediments from various sampling sites. Both of them have a relative coefficient of variation of less than 10% ( $n = 3$  for each).

### 3. Results and discussion

#### 3.1. DP distribution in marine sediments

As shown in Fig. 1, DP concentration in surface sediment samples ranged from 10 to 936 pg/g d.w. (dry weight) (average: 270 pg/g d.w.) in Pohang Bay and from 8 to 196 pg/g d.w. (average: 72 pg/g d.w.) in Busan Bay. The finding that Busan Bay had lower levels of DP than Pohang Bay was consistent with our previous study of PCDD/Fs in those areas, implying that Busan Bay was less contaminated (Lee et al., 2006). PCDD/Fs were generally from the byproduct of incomplete combustion and it is reasonable that Pohang Bay showed a higher PCDD/F emission due to coal burning during the steel-making process (Fang et al., 2011). In contrast, DP probably has a commercial source from its application in electrical devices and machines. It was also possible that the size-fraction of sediment might contribute the level of DP in the sediment, since elevated DP level was observed in the fine particle (see Section 3.2). However, Busan Bay (~83% by weight for size of  $<10 \mu\text{m}$ ) showed higher proportion of fine particles than Pohang Bay (~54% for size of  $<10 \mu\text{m}$ ), suggesting elevated level of DP in Pohang Bay was not due to higher fine particle fractions in the sediment. Therefore, the source of DP in South Korea should be characterized before any solid conclusion could be made. As expected, DP concentration decreased with increasing distance from land and industrial area. The highest concentration of DP was detected in areas closest to industrial effluent discharge, i.e. #2 (steel complex) in Pohang, #10 (shipyard) and #11 (port) in Busan Bay, indicating that urban and industrial activities appeared to be an important source of DP in marine sediment in South Korea.

The sediments obtained from both bays were examined to compare levels and isomeric profiles of DP with other studies (Table S4). The concentrations of DP in this study (0.01–0.94 ng/g d.w.) were slightly higher than those observed in the Songhua River (Qi et al., 2010) and Yellow Sea in China (Zhao et al., 2011), but much lower than those observed in sediments close to DP manufacturing sites such as Anpon (8 ng/g d.w.) (Wang et al., 2010), Lake Ontario (206 ng/g d.w.) and Lake Erie (30 ng/g d.w.) (Hoh et al., 2006). Due to limited samples in this study, further large scale investigation on the DP distribution in

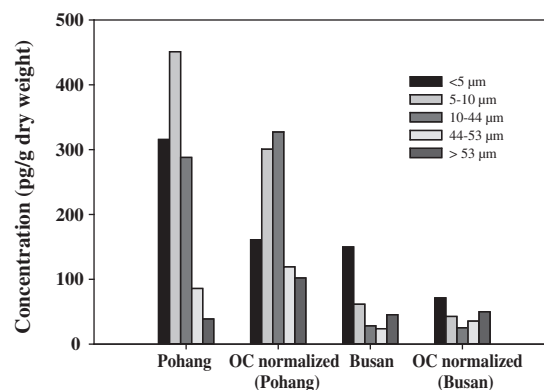
Korean sediment to characterize the contamination level of DP in South Korea is warranted.

#### 3.2. Distribution of DP in size-fractionated sediments

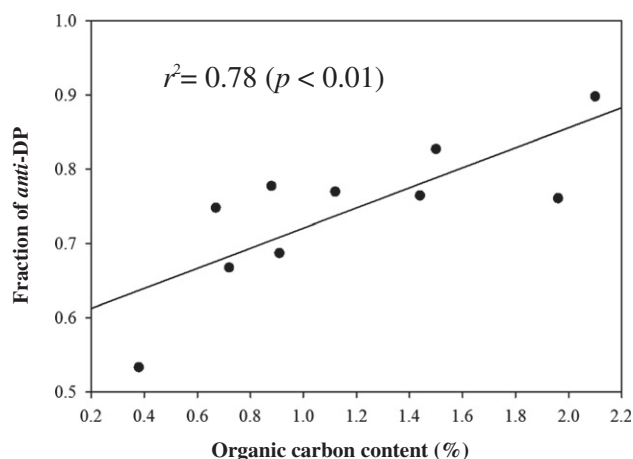
Concentrations of total DP in sediments of different particle sizes are given in Table S3 and shown in Fig. 2. DP was detected in all of the fractionated samples. The highest concentrations of DP were commonly detected in the two fine grain-sizes ( $<5$  and  $5\text{--}10 \mu\text{m}$ ), which are 451.2 and 149.9 pg/g d.w. for Busan and Pohang Bays; respectively. This shows a similar distribution to PCDD/Fs from our previous study (Lee et al., 2006). In Pohang Bay, DP concentration was highest in  $5\text{--}10 \mu\text{m}$  and  $10\text{--}44 \mu\text{m}$  (OC normalized). In Busan Bay, DP concentration and OC normalized were highest in  $<5 \mu\text{m}$ . The slightly different trend in both sites might be caused by the different sediment characterization at the two sites. In general, the OC normalized DP concentration showed a less discrepancy for both sediments, suggesting that OC would probably be a significant contributor for the high concentration of DP in the fine particles. Sverko et al. (2008) also suggested that the spatial distribution of DP in Lake Ontario was associated with fine-grained sediments. Since these fine particles were often food items of benthic organisms, elevated fine particle-bound DP is of great environmental concern.

#### 3.3. $f_{anti}$ in whole and size-fractionated sediments

To identify the source of DP in sediments,  $f_{anti}$  in the whole sediment and two fractionated samples of the two bays were investigated. It is of great significance to study  $f_{anti}$  profiles in different particle-

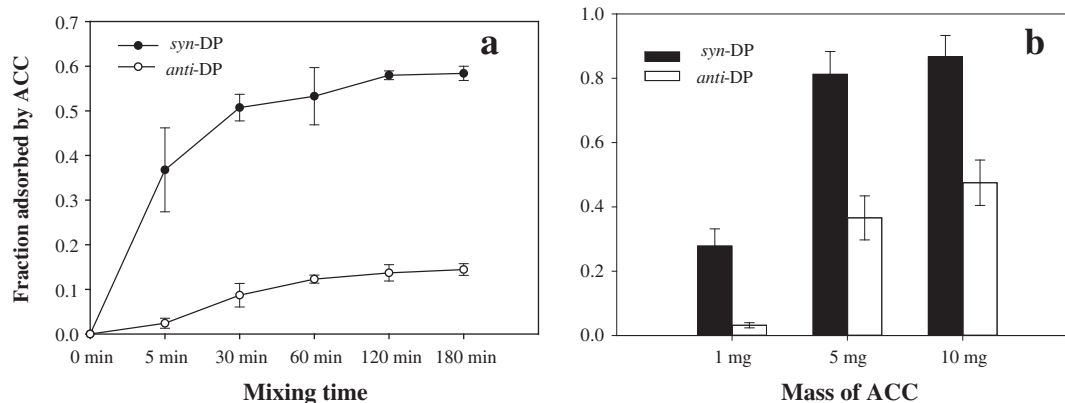


**Fig. 2.** DP concentration (pg/g d.w.) and OC normalized concentration ( $10^2$  pg/g OC) in two fractionated sediment samples in (a) Busan Bay and (b) Pohang Bay.



**Fig. 3.** Spearman correlation between  $f_{anti}$  and OC (%) in the two fractionated surficial sediment from Busan and Pohang Bays.

size fractions in one sediment, due to possibly the source and similar marine environment. The  $f_{anti}$  ranged from 0.75 to 0.86 and 0.76 to 0.81 for Busan Bay (average  $\pm$  sd:  $0.80 \pm 0.06$ ) and Pohang Bay (average  $\pm$  sd:  $0.79 \pm 0.06$ ); respectively. These ratios are consistent with the values reported in other sediment studies (Table S4). The  $f_{anti}$  of the commercial products produced by Oxychem ranged from 0.63 to 0.80 and was reported to be 0.60 in the Anpon, Jiangsu (Wang et al., 2010). Therefore, the enrichment of *anti*-DP was observed in those two bays. In the fractionated sub-samples (Table S2),  $f_{anti}$  has its highest value of 0.9 in  $<5 \mu\text{m}$  fraction (Pohang Bay) and the lowest 0.5 in  $>53 \mu\text{m}$  fraction (Busan Bay). In both fractionated sediments, the lowest  $f_{anti}$  was observed in the fraction with the largest particle size. Interestingly,  $f_{anti}$  significantly correlated with OC in the two fractionized sediment samples (Fig. 3). The enrichment of *anti*-DP over *syn*-DP could be attributable to higher adsorption of *anti*-DP by the sediment or preferential bio-degradation of *syn*-DP in the sediment. The latter was supported by the high  $f_{anti}$  in the fine particle, which should be more bioavailable to the microbe and benthic organisms and experience more biodegradation. Also, microbial activity and biomass has been found to be positively related with the OC in the soil and sediment, which might supply the nutrient source for the heterotrophic microbe (Hargrave, 1972; Mosher et al., 2006). In a previous sediment core study, a temporal increase of  $f_{anti}$  was observed with the passage of time, suggesting that the *anti*-isomer is more environmentally persistent than the *syn* isomer in sediment (Qiu et al., 2007).



**Fig. 4.** Fraction of *syn*-DP and *anti*-DP absorbed by: a) 5 mg ACC at different time points ( $n = 3$  for each); b) 1, 5, and 10 mg ACC after mixing for 3 days ( $n = 3$  for each). Error bars represent standard deviation of triplicates.

### 3.4. Adsorption of *anti*-DP and *syn*-DP by activated char carbon (ACC)

To investigate adsorption behaviors of *anti*-DP and *syn*-DP onto organic matter, well-controlled laboratory experiments should be conducted. However, such experiments were technically not feasible because DP is almost insoluble in aqueous solution due to its high  $\log K_{OW}$  and a long duration is required for DP to equilibrate between aqueous and sediment. Therefore, a simulated experiment design involving ACC as hydrophobic sorbent (resembling BC in sediment) (Allen-King et al., 2002; Kawashima et al., 2011) and methanol as hydrophilic solvent was developed, which has also been used in a previous study (Freundlich and Heller, 1939). Previous work has also revealed that BC has a stronger relationship with persistent organic pollutants (POPs, e.g. PAHs, PCBs and PCDD/Fs) than OC (Lohmann et al., 2005). Though no such evidence has been reported for DP, it is supposed that BC could also play a very important role in the sorption of DP due to its high  $\log K_{OW}$ . Therefore, we hypothesized that ACC used in this study can mimic the adsorption behavior of organic matter in sediment. To avoid background contamination,  $^{13}\text{C}$  labeled *syn*-DP and *anti*-DP were used and 15 ng of both were spiked into a series of 50 mL methanol in each glass centrifuge tube. Then 5 mg ACC (Sigma-Aldrich, 100 mesh), cleaned by DCM prior to use, was added to each tube and mixed on a roller mixer in dark. Triplicate control samples were prepared without adding ACC. Triplicate samples were collected at 5, 30, 60, 120 and 180 min, which were followed by centrifuge and separation of methanol from ACC.  $^{13}\text{C}$  labeled 2,2',3,3',4,4',5-heptachlorobiphenyl was added as internal standard to the decanted methanol in each tube and  $^{13}\text{C}$  labeled DP was analyzed. Adsorption rate was calculated by comparing to the triplicate control samples without adding ACC. To assess the effect of ACC amount, 1 mg, 5 mg, and 10 mg ACC ( $n = 3$  for each) was used and the recovery of  $^{13}\text{C}$  labeled DP was evaluated after mixing up to 3 days.

As shown in Fig. 4, adsorption of *syn*-DP by ACC was more than five times higher than that of *anti*-DP. After 3 h, approximate 60% of the spiked *syn*-DP was adsorbed; however, only 10% of *anti*-DP was adsorbed. This trend was also observed when different amount of ACC was used (Fig. 4(b)). During cleanup method development, we also found that *syn*-DP could be eluted with hexane in the multi-layer silica column, but only ~50% of *anti*-DP could be eluted with hexane, suggesting *anti*-DP has a lower solubility in non-polar organic solvent. These results indicated that *syn*-DP is more likely to be adsorbed by organic matter. The adsorption result in this study suggested that *syn*-DP is probably more hydrophobic than *anti*-DP, which is also consistent with the fact *syn*-DP is more bioaccumulative than *anti*-DP in a previous study (Tomy et al., 2008).

To tentatively explain the preferential adsorption of *syn*-DP by ACC,  $\log K_{OW}$ , a parameter determining adsorption should be investigated. However, to date, no experimental data on  $K_{OW}$  of DP have been



**Table 1**  
Calculated molecular descriptors of *syn*-DP and *anti*-DP using Gaussian 03 and Multiwfn.

|   | <i>Syn</i> -DP | <i>Anti</i> -DP |
|---|----------------|-----------------|
| Dipole moment (D)                         | 2.28           | 0               |
| Van der Waals volume (Bohr <sup>3</sup> ) | 3322           | 3314            |
| Maximum diameter (nm)                     | 1.24           | 1.42            |
| Minimum diameter (nm)                     | 0.52           | 0.56            |
| HOMO (kJ/mol)                             | −701           | −703            |
| LUMO (kJ/mol)                             | −135           | −134            |
| Internal energy (kJ/mol)                  | −14,453,867    | −14,453,880     |

reported. Thus, we tried to compare the  $\log K_{OW}$  through the retention time index in liquid chromatography (LC) columns, which has been validated in previous studies (Zhang et al., 1999). *Anti*-DP was eluted ~0.7 min earlier than *syn*-DP in Restek Pinnacle DB Biphenyl column and methanol/water as mobile phase (Zhou et al., 2011). Greg et al. (Tomy et al., 2008) also observed *anti*-DP were eluted ~3 min ahead of *syn*-DP using isocratic condition in the C18 LC column, confirming the *syn*-DP was probably more hydrophobic than *anti*-DP, i.e., higher  $\log K_{OW}$ . This difference in hydrophobicity was also reflected in the different aqueous solubility of the two isomers at 207 ng/L and 572 ng/L, though which DP isomer has a lower or higher aqueous solubility is not specified (2004). The estimated higher  $\log K_{OW}$  of *syn*-DP was consistent with the preferential adsorption of *syn*-DP by the ACC and higher bioaccumulation factor of *syn*-DP in fish (Tomy et al., 2008). In this study, we also found that *syn*-DP was eluted ~0.7 min earlier than *anti*-DP in DB-5HT GC column, suggesting that *syn*-DP possibly had a lower octanol-air partitioning coefficient ( $\log K_{OA}$ ) than that of *anti*-DP (Hayward et al., 2006). The  $\log K_{OA}$  difference can also affect LRT of DP, which might partly contribute to the decreased  $f_{anti}$  during LRT (Möller et al., 2010). For example, the ratio of heavier PCDD/Fs with high  $\log K_{OA}$  decreases during LRT due to the preferential deposition of heavier ones, which are primarily partitioned to particles (Lohmann

and Jones, 1998). However, no certain conclusion could be made until the direct measurement of those physicochemical properties was conducted.

### 3.5. Calculation of molecular descriptors of *anti*- and *syn*-DP using Gaussian 03

To further explain the different adsorption behaviors and bioaccumulation of DP isomers, several important molecular descriptors related with adsorption were computed with Gaussian 03. Geometry optimization of *anti*- and *syn*-DP was calculated using density functional theory (DFT) method with the restrict B3-LYP exchange-correlation functional. In these calculations, 6-31G(d) basis sets were adopted to all atoms. No symmetry constraints were applied on each compound. After the geometry optimization of *anti*-DP and *syn*-DP (Fig. S1), a user-friendly Gaussian 03 based Multiwfn program (Lu and Chen, 2012) was used to view the molecular size, and calculate the dipole moment, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), internal energy and the Van der Waals volume (Table 1). As shown in Fig. 5, cross-sectional diameters including maximal diameter, effective diameter (the second minimum diameter) and minimum diameter were manually measured. When calculating Van der Waals volume, (*i*, *x*, *k*) input started with (9, 0.002, 1.7) by increasing *i* gradually until the result variation between *i* and *i* + 1 was small enough to be acceptable as converged. The calculation result showed no significant difference on HOMO, LUMO and internal energy of the two isomers. However, the dipole moment of *syn*-DP (2.28) was higher than that of *anti*-DP (0), which is consistent with more rotationally symmetric molecular structure of *anti*-DP. Van der Waals volume of *anti*-DP (3314 Bohr<sup>3</sup>) was slightly smaller than that of *syn*-DP (3322 Bohr<sup>3</sup>), which might partly explain the higher hydrophobicity of *syn*-DP due to the fact that smaller molecular tended to be more soluble in the water (Moriguchi, 1975). However, the maximal cross-sectional diameter of *syn*-DP (1.24 nm) was smaller than that of *anti*-DP (1.42 nm).

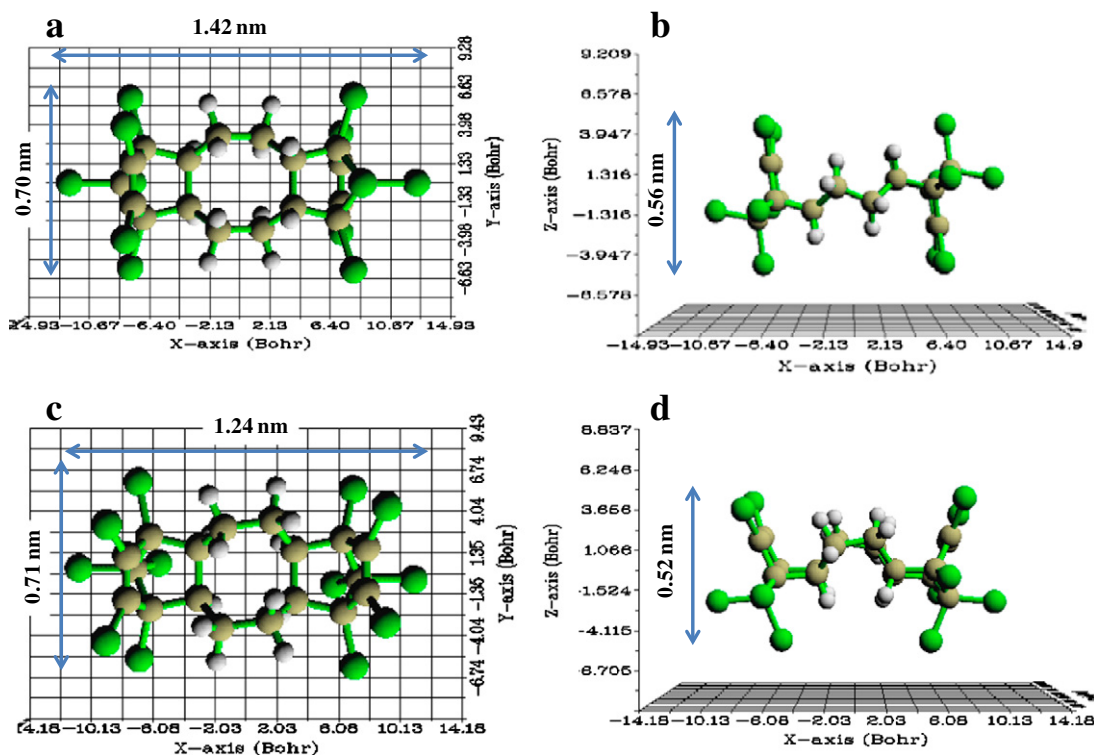


Fig. 5. Cross-sectional diameters for (a) X-Y plane of *anti*-DP; (b) X-Z plane of *anti*-DP; (c) X-Y plane of *syn*-DP; (d) X-Z plane of *syn*-DP.

Furthermore, a “dummy dihedral angle” model expressing the departure of the molecules line of symmetry from planarity was constructed to demonstrate the extensiveness of the molecular structure and explain the molecular size difference between DP isomers (Fig. S2).

### 3.6. Implication of isomer-specific environmental and biological fates

Enrichment of *anti*-DP in the coastal sediment can either be caused by preferential adsorption of *anti*-DP or higher biodegradation rates of *syn*-DP, since long range transport was negligible. However, simulated ACC adsorption test had revealed an opposite fact that *syn*-DP was preferentially adsorbed due to higher  $\log K_{OW}$  of *syn*-DP. Although *anti*-DP has a lower dipole moment than that of *syn*-DP, hydrophobicity, as described by  $\log K_{OW}$ , is a bulk property of the chemical, and could also be affected by other molecular structure parameters such as molecular size. As mentioned above, slightly smaller molecular volume of *anti*-DP is likely to decrease its hydrophobicity by increasing the aqueous solubility. Furthermore, the structure of ACC primarily consists of layers of graphene sheets arranged in a random manner to generate a microporous system (<2 nm) and accessibility of a sorbate to the pore was also affected by its molecular size (Zhu and Pignatello, 2005). Therefore, it might occur that the larger molecular diameter of *anti*-DP than that of *syn*-DP reduce its accessibility to the micropores. The higher uptake rates of *syn*-DP than *anti*-DP in the fish might also be explained by smaller maximal diameter of *syn*-DP. For the hydrophobic compounds which has a  $\log K_{OW}$  larger than 6, the molecular size is usually the dominating factor that controls its uptake rate in the gas-intestinal tract (Dimitrov et al., 2002). A threshold value of about 1.5 nm for maximal cross-sectional diameter has been found to discriminate chemicals with  $\log BCF$  (bioconcentration factor) > 3.3 from  $\log BCF$  < 3.3. Since DP has an estimated nonisomer specific  $\log K_{OW}$  of 11.2, it is believed that both DP have a  $\log K_{OW}$  over than 6. The calculated maximal diameter of *anti*-DP is 1.42 nm, close to the cutoff limit of 1.5 nm, is greater than that of *syn*-DP with a diameter of 1.24 nm. As shown in Fig. S3, BCF decreases with increasing molecular size and the BCF range of the smaller *syn*-DP can be one to two orders of magnitude higher than that of *anti*-DP. In conclusion, the fact that *syn*-DP is preferentially adsorbed by the hydrophobic sorbent and higher  $f_{anti}$  in the smaller particles indirectly supported the hypothesis that the enrichment of *anti*-DP in the marine sediment was probably due to preferential biodegradation of *syn*-DP. However, further studies on the isomer specific biodegradation of DP should be conducted to confirm this hypothesis.

### Conflict of interest

This paper declares no conflict of interest.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2014.01.082>.

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